

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-180325

(43)Date of publication of application : 26.06.2002

(51)Int.Cl.

D01F 6/26

D01F 6/22

(21)Application number : 2000-381369

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(22)Date of filing : 15.12.2000

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IGARASHI ICHIRO**(54) FIBROUS FORMED PRODUCT****(57)Abstract:**

PROBLEM TO BE SOLVED: To produce a flexible synthetic fiber of high mechanical strength with high heat resistance and chemical resistance.

SOLUTION: The objective fibrous formed product is obtained by spinning a polymer having a melting point, wherein the polymer is characterized by being a norbornene-based ring-opened polymer, a norbornene-based ring-opened polymer's hydrogenated product or a styrene-based polymer's hydrogenated product containing syndiotactic structure.

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CLAIMS

[Claim(s)]

[Claim 1]Fibrous mold goods, wherein it is fibrous mold goods which carry out spinning of the polymer which has the melting point and said polymer is a norbornene system ring-opening-polymerization object, a norbornene system ring-opening-polymerization object hydride, or a syndiotactic structure content styrene system polymer hydride.

[Claim 2]said norbornene system ring-opening-polymerization object -- the inside of all the polymer repeating units -- a repeating unit of norbornene system monomer origin of three or more ring formations -- more than 10 mol % -- the fibrous mold goods according to claim 1 which are what is contained.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention about the fibrous mold goods of the hydride of a norbornene system ring-opening-polymerization object and this ring-opening-polymerization object, or a syndiotactic structure content styrene system polymer hydride in more detail, It excels in heat resistance and chemical resistance, and is related with the fibrous mold goods of the norbornene system ring-opening-polymerization object which is high intensity, this ring-opening-polymerization object hydride, or a syndiotactic structure content styrene system polymer hydride.

[0002]

[Description of the Prior Art]As a synthetic fiber which consists of thermoplastics until now, polyvinyl alcohol, Flexibility polymer fibers of the structure where an amorphism part intervenes between crystal parts, such as polyethylene, polypropylene, polyethylene terephthalate, and polyamide, consider it as the textiles which combine aesthetic property and a mechanical strength moderate, and are widely used for industrial use, such as an object for garments, a fishing net, a rope. However, each of these was insufficient heat resistance and in respect of chemical resistance. On the other hand, syndiotactic polystyrene textiles were proposed as textiles which improve heat resistance and chemical resistance (JP,1-183516,A). However, neither heat resistance nor chemical resistance is yet enough, and an improvement of intensity is desired by this.

[0003]

[Problem(s) to be Solved by the Invention]Without spoiling aesthetic property, the purpose of this invention is excellent in heat resistance and chemical resistance, and there is in providing the textiles which are high intensity.

[0004]

[Means for Solving the Problem]. Have the melting point, as a result of inquiring wholeheartedly, in order that this invention persons may solve said technical problem. Textiles which carry out spinning of a norbornene system ring-opening-polymerization object, a norbornene system ring-opening-polymerization object hydride, or the syndiotactic structure content styrene system polymer hydride find out suiting the above-mentioned purpose, and came to complete this invention based on this knowledge. They are fibrous mold goods which carry out spinning of the polymer which has (1) melting point in this way according to this invention, Fibrous mold goods, wherein said polymer is a norbornene system ring-opening-polymerization object, a norbornene system ring-opening-polymerization object hydride, or a syndiotactic structure content styrene system polymer hydride, (2) -- said norbornene system ring-opening-polymerization object -- the inside of all the polymer repeating units -- a repeating unit of norbornene system monomer origin of three or more ring formations -- more than 10 mol % -- the above (1) which is what is contained is provided with fibrous mold-goods ** of a statement. [and]

[0005]moreover -- as a desirable mode -- (3) -- fibrous mold goods the above (1) in which said polymer is a norbornene system ring-opening-polymerization object hydride, or given in (2). (4) Fibrous mold goods given in either of above-mentioned (1) - (3) whose weight average molecular

weight measured with gel permeation chromatography of said norbornene system ring-opening-polymerization object or its hydride is 500-1,000,000 in polystyrene conversion, (5) Said norbornene system ring-opening-polymerization object hydride or a syndiotactic structure content styrene system polymer hydride, Fibrous mold goods given in either of above-mentioned (1) - (4) produced by hydrogenating not less than 50% of carbon-carbon double bonds, And either of (6) above-mentioned [the above-mentioned melting point of said norbornene system ring-opening-polymerization object, this polymer hydride, or a syndiotactic structure content styrene system polymer hydride is 130-400 **] (1) - (5) is provided with fibrous mold-goods ** of a statement.

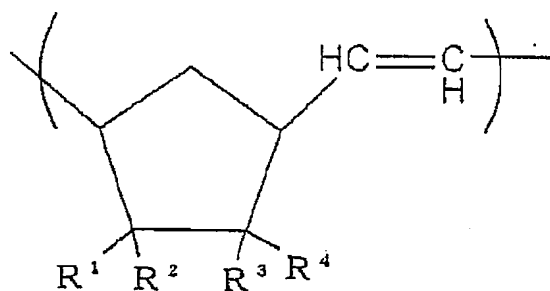
[0006]

[Embodiment of the Invention]The norbornene system ring-opening-polymerization object used by this invention is a polymer produced by carrying out ring opening polymerization of the monomer which has a norbornene ring. This norbornene system ring-opening-polymerization object is the gel permeation chromatography (polystyrene conversion) with which the weight average molecular weight (Mw) uses chloroform as a solvent, 500-1,000,000 -- desirable -- 1,000-600,000 -- it is 5,000-400,000 more preferably. [usually,] When Mw is too low, there is a possibility that the mechanical strength of fibrous mold goods may fall, on the other hand, if Mw is too high, melting mobility may get worse and spinning may become difficult. Unlike the conventional norbornene system ring-opening-polymerization object, the norbornene system ring-opening-polymerization object used for this invention has the melting point (it may be hereafter described as Tm.). The melting point is a temperature which the crystal part of a polymer dissolves. Generally measurement of the melting point can be performed based on the endothermic peak which originates in fusion of the crystal component of a polymer using a differential scanning calorimeter. The melting point of this norbornene system ring-opening-polymerization object is usually 130-400 ** between 200 ** - 400 ** preferably.

[0007]a suitable norbornene system ring-opening-polymerization object to use for this invention -- the repeating unit of the norbornene system monomer origin of three or more ring formations (a) -- the inside of all the repeating units -- 10 - 100-mol % -- it contains. The norbornene system monomer of three or more ring formations is a norbornene system monomer which has one or more rings in addition to a norbornene ring (it is 2 **** rare ** to this), and is a dicyclopentadiene preferably. As a repeating unit of this monomer origin (a), the repeating unit shown in the circular parenthesis in a following general formula (1) or (2) is mentioned, for example.

[0008]

[Formula 1]

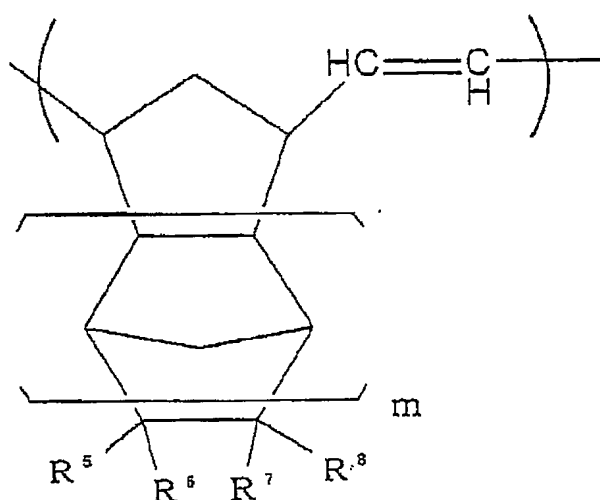


(1)

[0009]the inside of a formula, $R^1 - R^4$ -- respectively -- independent -- a hydrogen atom. The substituent containing the hydrocarbon group or the halogen atom, the silicon atom, oxygen atom, or nitrogen atom of the carbon numbers 1-20 may be expressed, and R^1 or R^2 , R^3 , or R^4 may form the ring which was combined mutually and the hydrocarbon group of the carbon numbers 1-40 combined.

[0010]

[Formula 2]



[0011]the inside of a formula, $R^5 - R^8$ — respectively — independent — a hydrogen atom and the hydrocarbon group of the carbon numbers 1-20. Or the substituent containing a halogen atom, a silicon atom, an oxygen atom, or a nitrogen atom may be expressed, and R^5 or R^6 , R^7 , or R^8 may form the ring which was combined mutually and the hydrocarbon group of the carbon numbers 1-40 combined. m is 1 or 2.

[0012]Although the norbornene system ring-opening-polymerization inside of the body may have a repeating unit of monomer origin of those other than a norbornene system monomer, in this invention a repeating unit of norbornene system monomer origin, desirable — more than 20 mol % — more — desirable — more than 50 mol % — poor occurrence frequency of crystalline textiles becomes low, and what is contained is preferred. A norbornene system ring-opening-polymerization object hydride used for this invention is obtained by making hydrogen add to a carbon-carbon double bond which exists in a main chain or/and a side chain of a polymer produced by carrying out ring opening polymerization of the monomer which has the above-mentioned norbornene ring.

[0013]This norbornene system ring-opening-polymerization object hydride is the gel permeation chromatography (polystyrene conversion) with which the weight average molecular weight (M_w) uses chloroform as a solvent, 500-1,000,000 — desirable — 1,000-600,000 — it is 5,000-400,000 more preferably. [usually,] When M_w is too low, there is a possibility that a mechanical strength of mold goods may fall, conversely, if M_w is too high, melting mobility may get worse and a fabricating operation may become difficult. Unlike the conventional norbornene system ring-opening-polymerization object hydride, a norbornene system ring-opening-polymerization object hydride used for this invention has the melting point. The melting point is a temperature which a crystal part of a polymer dissolves. It can ask for the melting point with the above-mentioned measuring method etc. 130 ** - 400 ** of $T_m(s)$ of this norbornene system ring-opening-polymerization object hydride are usually among 200-400 ** preferably.

[0014]A suitable norbornene system ring-opening-polymerization object hydride to use for this invention, a repeating unit of norbornene system monomer origin — the inside of all the repeating units — 10-100-mol % — desirable — 50-100-mol % — especially — desirable — 70-100-mol % — it is a ring-opening-polymerization object to contain, and is a hydride usually produced by adding hydrogen to not less than 50% of the carbon-carbon double bond. A norbornene system ring-opening-polymerization object used for this invention and its hydride (henceforth, these both may be named generically and it may be called "norbornene system resin".) can carry out ring opening polymerization of the norbornene system monomer, and can hydrogenate and obtain it if needed.

[0015]As a norbornene system monomer for obtaining norbornene system resin, Norbornene, 5-methyl norbornene, 5-ethyl norbornene, 5-butyl norbornene, 5-hexyl norbornene, 5-decyl

norbornene, Norbornene;5-ethylidene norbornene which has no replacing or alkyl groups, such as 5-cyclohexyl norbornene and 5-cyclopentyl norbornene, Norbornene which has aromatic rings, such as norbornene;5-phenyl norbornene which has alkenyl groups, such as 5-vinyl norbornene, 5-propenyl norbornene, 5-cyclohexenyl norbornene, and 5-cyclopentenyl norbornene; [0016]5-carbomethoxy norbornene, 5-ethoxycarbonyl norbornene, 5-methyl-5-carbomethoxy norbornene, 5-methyl-5-ethoxycarbonyl norbornene, Knoll *****- 2-methylpropionate, Knoll *****- 2-methylocta NEITO, A norbornene 5,6-dicarboxylic anhydride, 5-hydroxymethyl norbornene, 5,6-JI (hydroxymethyl) norbornene, 5,5-JI (hydroxymethyl) norbornene, 5-hydroxy isopropyl norbornene, 5,6-dicarboxy norbornene, The norbornene which has a polar group containing oxygen atoms, such as 5-carbomethoxy-6-carboxy norbornene; the norbornene which have a polar group containing nitrogen atoms, such as 5-cyano norbornene and norbornene 5,6-imidodicarboxylate, is mentioned.

[0017]In this invention, a suitable norbornene system monomer is a polycyclic type norbornene system monomer (a') of three or more ring formations. As an example of a polycyclic type norbornene system monomer (a') of three or more ring formations, A dicyclopentadiene or tricyclo [4.3.0.1^{2,5}] dec-3-ene which saturated a double bond of a five-membered ring portion of a dicyclopentadiene, tricyclo [4.4.0.1^{2,5}] *****- 3-ene, etc. can be mentioned. Tetracyclo [6.5.0.1^{2,5}.0^{8,13}] trideca- 3,8,10,12-tetraene (it is also called a 1,4-methano-1,4,4 a,9a-tetrahydro fluorene), Norbornene derivative which has aromatic rings, such as tetracyclo [6.6.0.1^{2,5}.0^{8,13}] tetradeca- 3,8,10,12-tetraene (it is also called the 1,4-methano- 1, 4, 4a, 5, and 10 and 10a-hexahydroanthracene);

[0018]Tetracyclo dodecen, 8-methyltetracyclo dodecen, 8-ethyltetracyclo dodecen, Tetracyclododecene;8-methylidene tetracyclo dodecen which has no replacing or alkyl groups, such as 8-cyclohexyl tetracyclo dodecen and 8-cyclopentyl tetracyclo dodecen, 8-ethylidene tetracyclo dodecen, 8-vinyl tetracyclo dodecen, 8-propenyl tetracyclo dodecen, 8-cyclohexenyl tetracyclo dodecen, Tetracyclododecene which has a double bond in norbornene exocyclic, such as 8-cyclopentenyl tetracyclo dodecen; tetracyclododecene which has aromatic rings, such as 8-phenyl tetracyclo dodecen;

[0019]8-carbomethoxy tetracyclo dodecen, 8-methyl-8-carbomethoxy tetracyclo dodecen, 8-hydroxymethyl tetracyclo dodecen, 8-carboxy tetracyclo dodecen, Tetracyclododecene;8-cyano tetracyclo dodecen which has a substituent containing oxygen atoms, such as tetracyclo dodecen 8,9-dicarboxylic acid and a tetracyclo dodecen 8,9-dicarboxylic anhydride, The tetracyclo dodecen 8, Nitrogen atoms, such as 9-imidodicarboxylate. Tetracyclododecene which has a substituent containing halogen atoms, such as tetracyclododecene;8-chloro tetracyclo dodecen which has an included substituent; tetracyclododecene which has a substituent containing silicon atoms, such as 8-trimethoxysilyl tetracyclo dodecen;

[0020]Hexacycloheptadecen, 12-methylhexacycloheptadecen, 12-ethyl hexacycloheptadecen, 12-cyclohexyl hexacycloheptadecen, The hexacycloheptadecen which has no replacing or alkyl groups, such as 12-cyclopentyl hexacycloheptadecen; 12-methylidene hexacycloheptadecen, 12-ethylidene hexacycloheptadecen, 12-vinyl hexacycloheptadecen, 12-propenyl hexacycloheptadecen, 12-cyclohexenyl hexacycloheptadecen, The hexacycloheptadecen which has a double bond in exocyclic [, such as 12-cyclo PENTENIRUHEKISA cyclohexa decene,]; hexacycloheptadecen which has aromatic rings, such as 12-phenyl hexacycloheptadecen;

[0021]12-carbomethoxy hexacycloheptadecen, 12-methyl-12-carbomethoxy hexacycloheptadecen, 12-hydroxymethyl hexacycloheptadecen, 12-carboxy hexacycloheptadecen, Hexacycloheptadecen;12-cyano hexacycloheptadecen which has a substituent containing oxygen atoms, such as hexacycloheptadecen 12,13-dicarboxylic acid and a hexacycloheptadecen 12,13-dicarboxylic anhydride, The hexacycloheptadecen 12,13-imidodicarboxylate; Hexacycloheptadecen; which has a substituent which contains an atom for halogen, such as 12-chloro hexacycloheptadecen. The hexacycloheptadecen which have a substituent containing silicon atoms, such as 12-trimethoxysilyl hexacycloheptadecen, is mentioned.

[0022]A thing of three ring formations or four ring formations is preferred at a point that the

crystallinity of a polymer becomes high also in these, A dicyclopentadiene which does not have straight chain shape or a branched state substituent especially, Tricyclo [4.3.0.1^{2,5}]-dec-3-ene, tetracyclo [6.5.0.1^{2,5}.0^{8,13}] trideca- 3,8,10,12-tetraene, Tetracyclo [6.6.0.1^{2,5}.0^{8,13}] tetradeca- 3,8,10,12-tetraene, tetracyclo dodecen, and 8-methyltetracyclo dodecen are still more preferred, and especially a dicyclopentadiene is preferred.

[0023]The body and an isomer of exo** are contained in the above-mentioned monomer. A monomer for obtaining norbornene system resin used for this invention, Although it may be a mixture of these isomers, in order to improve crystallinity more, in an isomeric mixture, 70% of the weight or more of a thing is preferred for 70% of the weight or more of a thing or exo**, one of a thing which has high composition ratio, i.e., an end object, of an isomer ingredient.

Copolymerization of the norbornene system monomer can be carried out to it and copolymerizable cyclic olefin. Cyclic olefin of a monocycle is mentioned as copolymerizable cyclic olefin. The cyclic olefin of a monocycle is cyclic olefin or diolefins, and these substitution products of C4 - C20, and it is cyclic olefin or diolefins, and these derivatives of C4 - C10 preferably.

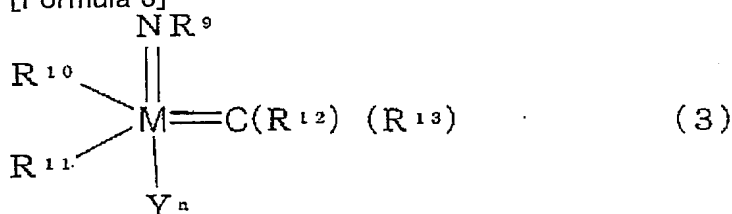
[0024]As an example of the cyclic olefin of a monocycle, or diolefins, Cyclobutene, cyclopentene, methylcyclopentene, a cyclohexene, A cyclic olefin system monomer of a monocycle indicated to JP,64-66216,A, such as a methylcyclohexene, cyclohepten, and cyclooctane, etc.;

Cyclohexadiene, An annular diolefin system monomer indicated to JP,7-258318,A, such as methylcyclohexadiene, cyclo-octadiene, methyl cyclo-octadiene, and phenyl cyclo-octadiene, etc. can be mentioned.

[0025]A suitable polymerization catalyst used in order to obtain norbornene system resin which is used by this invention, and which has the melting point, A compound which has at least one imido group combined with the 6th group transition metal of the periodic table, and has at least one substituent further chosen from a group which consists of an alkoxy group, an aryloxy group, an alkylamide group, and an aryl amide group is contained as the main ingredients. Specifically, it is a following general formula (3).

[0026]

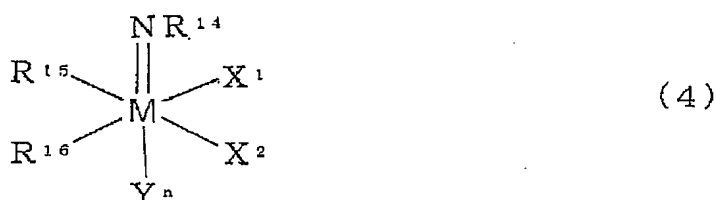
[Formula 3]



[0027](R⁹ expresses an alkyl group or an aryl group among a formula, and R¹⁰ and R¹¹ express an alkoxy group, an aryloxy group, an alkylamide group, or an aryl amide group independently mutually.) R¹⁰ and R¹¹ may be combined mutually. R¹² and R¹³ express hydrogen, alkyl group, or aryl group which carried out mutually-independent, An alkyl group is a straight chain of the carbon numbers 1-20, a branched-chain alkyl group, or a cycloalkyl group of the carbon numbers 3-20 preferably, for example, a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, a tert-butyl group, or a cyclohexyl group is mentioned. An aryl group is a thing of the carbon numbers 6-20 preferably, for example, are 1 which has a substituent in either a phenyl group, 2, 3, 4 and 5 or the 6th place - a 5 substituted-phenyl group. Y is electron-donative neutral ligand and n is an integer of 0-2. N is nitrogen and M is a transition metal chosen from the 6th fellows of the periodic table. And following general formula (4)

[0028]

[Formula 4]



[0029] R^{14} expresses an alkyl group or an aryl group among a formula, and R^{15} and R^{16} express an alkoxy group, an aryloxy group, an alkylamide group, or an aryl amide group independently mutually.) R^{15} and R^{16} may be combined mutually. X^1 and X^2 express halogen, the alkyl group, aryl group, or alkyl silyl group which carried out mutually-independent, Y is electron-donative neutral ligand, and n is an integer of 0-2. N is nitrogen and M is a transition metal chosen from the 6th fellows of the periodic table. It can mention.

[0030] R^9 of a general formula (3) and R^{14} of a general formula (4), Like [are an alkyl group or an aryl group and] the alkyl group or aryl group in R^{12} and R^{13} of a general formula (3), An alkyl group is a straight chain of the carbon numbers 1-20, a branched-chain alkyl group, or a cycloalkyl group of the carbon numbers 3-20 preferably, for example, a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, a tert-butyl group, or a cyclohexyl group is mentioned. An aryl group is a thing of the carbon numbers 6-20 preferably, for example, are 1 which has a substituent in either a phenyl group, 2, 3, 4 and 5 or the 6th place - a 5 substituted-phenyl group. R^{10} , R^{11} , R^{15} , and R^{16} are an alkoxy group, an aryloxy group, an alkylamide group, or an aryl amide group. Said alkoxy group is a thing of the carbon numbers 1-20 preferably, for example, a methoxy group, an ethoxy basis, a propoxy group, an isopropoxy group, a butoxy group, a tert-butoxy group, or a cyclohexyl group is mentioned. Aryloxy groups are 1 which has a substituent in either a phenoxy group, 2, 3, 4 and 5 or the 6th place - 5 substitution phenoxy group preferably, for example.

[0031] As a substituent which said substituted phenyl group and a substitution phenoxy group have, A methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, a tert-butyl group, An alkyl group or cycloalkyl groups, such as a cyclohexyl group; A phenyl group, Aryl groups, such as a naphthyl group; The alkyl silyl which has an alkyl group or aryl groups, such as a trimethylsilyl group and a dimethylphenyl silyl group, or alkyl aryl silyl; fluoride, Alkoxy group; cyano groups, such as halogen; methoxy groups, such as chlorine, bromine, or iodine, an ethoxy basis, and a propoxy group; 1 which has a naphthyl group or the same substituent as the above to either of the 2-8th place - 8 substitution naphthyl group, etc. are mentioned.

[0032] Furthermore, as an alkylamide group or an aryl amide group, A carbon number of an alkylamide group of the carbon numbers 1-20 of an alkyl group or an aryl group is an aryl amide group of 6-20 preferably, For example, a N,N-dimethyl amide group, N-methyl (N-tert-butyl) amide group, N-methyl (N-trimethylsilyl) amide group, an N-phenyl-N-methylamide group, N-phenyl (N-trimethylsilyl) amide group and N-(2,6-dimethylphenyl)- N-methylamide group. N-(2,6-diisopropylphenyl)- N-methylamide group, an N-(2,6-dimethylphenyl)-N-(trimethylsilyl) amide group, an N-(2,6-diisopropylphenyl)-N-(trimethylsilyl) amide group, etc. are mentioned.

[0033] As a polymerization catalyst for obtaining norbornene system resin used by this invention, what R^{10} , R^{11} or R^{15} , and R^{16} in a formula (3) or (4) have combined mutually is much more preferred. As a mutually united alkoxy group or an aryloxy group, a propyl-1,3-dioxy group, butyl-1,4-dioxy group, cyclohexyl-1,2-dimethoxy group, 2, and 2'-biphenoxy group, 1, and 1-bis-2-naphthoxy group etc. are mentioned. As an alkylamide group or an aryl amide group, A 1,3-propyl-N,N'-dimethyldiamide group, a 1,3-propyl-N,N'-JI (trimethylsilyl) diamide group, a 1,3-propyl-bis(phenylamide)basis, a N,N'-bis(trimethylsilyl)-2,2'-biphenyl diamide group, etc. are mentioned.

[0034] R^{12} and R^{13} of a general formula (3) are hydrogen, an alkyl group, or an aryl group. A desirable thing of an alkyl group or an aryl group is the same as that of a desirable thing of an alkyl group of R^9 of the above-mentioned general formula (3), and R^{14} of a general formula (4), or

an aryl group. X^1 and X^2 of a general formula (4) are halogen, an alkyl group, an aryl group, or an alkyl silyl group. A desirable thing in case X^1 or X^2 is an alkyl group or an aryl group is the same as that of R^9 of the above-mentioned general formula (3), and a desirable thing of an alkyl group of R^{14} of a general formula (4), or an aryl group. As for a desirable example in case X^1 or X^2 is halogen, fluoride, chlorine, bromine, and iodine are mentioned. As a desirable example in case X^1 or X^2 is an alkyl silyl group, the alkyl silyl of 1-20 (an aryl group of the carbon numbers 6-20 may also be included) is mentioned for a carbon number of alkyl groups, such as a trimethylsilyl group and a dimethylphenyl silyl group.

[0035]Y of a general formula (4) is electron-donative neutral ligand, is an electron donative compound which generally has a hetero atom, and, specifically, can mention phosphines, ether, amines, etc. As phosphines, trimethyl phosphine, triisopropyl phosphine, . Aryl groups of the carbon numbers 6-20, such as tri-cyclohexyl phosphine and triphenyl phosphine, may be contained. a carbon number of an alkyl group -- trialkylphosphine of 1-20, or a carbon number of an aryl group -- doria of 6-20 -- reel phosphine, [mention and] Diethylether, a tetrahydrofuran, 1,2-dimethoxyethane, etc. are mentioned as ether, and trialkylamine, such as trimethylamine and triethylamine, pyridine, a lutidine, etc. are mentioned as amines.

[0036]An organic metal reducing agent may be added to the above-mentioned polymerization catalyst, and it may polymerize in it in order to raise polymerization activity. The organic metal reducing agent can mention an organic metallic compound of the periodic table 1st which has a hydrocarbon group of the carbon numbers 1-20, 2, 12 and 13, or 14 fellows. Especially, organic lithium, organic magnesium, organic zinc, organic aluminium, and organic tin are preferred, and organic aluminium and especially organic tin are preferred. n-butyl lithium, methyl lithium, phenyllithium, etc. can be mentioned as organic lithium. As organic magnesium, butylethylmagnesium, butyloctylmagnesium, dihexylmagnesium, ethylmagnesiumchloride, n-butylmagnesiumchloride, allylmagnesiumbromide, etc. can be mentioned. Dimethyl zinc, diethylzinc, diphenylzinc, etc. can be mentioned as organic zinc. Trimethylaluminum, triethylaluminum, triisobutylaluminum, a diethylaluminium chloride, etc. can be mentioned as organic aluminium. n-butyltin, tetraphenyltin, etc. can be mentioned as organic tin.

[0037]As for quantity which adds an organic metal reducing agent, 0.1 to 100 times are preferred to a central metal of a polymerization catalyst, its 0.2 to 50 times are more preferred, and especially its 0.5 to 20 times are preferred. Polymerization activity of an addition does not improve in 0.1 or less time, but a side reaction occurs easily that they are 100 or more times. a rate of a polymerization catalyst over a monomer -- a mole ratio of a transition metal versus a monomer in a polymerization catalyst -- usually -- 1:100 to 1:2,000,000 -- desirable -- 1:500 to 1:1,000,000 -- it is 1:1,000-1:500 and 000 more preferably. If there are too many catalyst amounts, catalyst removal after a polymerization reaction will become difficult, and if too small, sufficient polymerization activity will not be acquired.

[0038]In order to adjust a molecular weight of a norbornene system ring-opening-polymerization object, adequate amount addition of a vinyl compound or the diene compound can be carried out as a regulator. As a vinyl compound or a diene compound used for a regulator, For example, alpha olefins, such as 1-butene, 1-pentene, 1-hexene, and 1-octene; Styrene, Styrene, such as vinyltoluene; Ethyl vinyl ether, isobutylvinyl ether, ether [, such as allyl glycidyl ether,]; -- containing halogen vinyl compound [, such as an allyl chloride,]; -- oxygen content vinyl compound [, such as glycidyl methacrylate]; -- nitrogen content vinyl compound [, such as acrylamide]; -- 1,4-pentadiene and 1,4-hexadiene. 1,5-hexadiene, 1,6-heptadiene, 2-methyl-1,4-pentadiene, Conjugated dienes, such as nonconjugated diene, such as 2,5-dimethyl-1,5-hexadiene, or 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, and 1,3-hexadiene, etc. can be mentioned. The quantity of a vinyl compound or a diene compound should just be a quantity which is sufficient for obtaining a polymer with a desired molecular weight, and is usually 0.1-10-mol % to a monomer.

[0039]In a polymerization for obtaining norbornene system resin used for this invention, although it can also react with a non-solvent, when performing a hydrogenation reaction, and when

continuing after a polymerization and performing wet spinning, since polymerizing in an organic solvent becomes possible [that a solvent can also be used in common], it is desirable after a polymerization. Especially if a polymer and a polymer hydride dissolve or distribute an organic solvent used by said polymerization reaction on condition of predetermined and a polymerization and a hydrogenation reaction are not influenced, it will not be limited, but a solvent currently industrially used widely is preferred. As such an organic solvent, for example Aliphatic hydrocarbon; cyclopentanes, such as pentane, hexane, and heptane, Cyclohexane, a methylcyclohexane, dimethylcyclohexane, Trimethylcyclohexane, ethylcyclohexane, diethylcyclohexane, Decahydronaphthalene, bicycloheptane, tricyclodecane one, hexahydro indene cyclohexane, Alicycle fellows hydrocarbon, such as cyclooctane; Aromatic hydrocarbon; dichloromethanes, such as benzene, toluene, and xylene, Halogen system aliphatic hydrocarbon, such as chloroform and 1,2-dichloroethane; Chlorobenzene, Halogen system aromatic hydrocarbon, such as dichlorobenzene; although solvents, such as ether, such as nitrogen-containing hydrocarbon; diethylether, such as nitromethane, nitrobenzene, and acetonitrile, and a tetrahydrofuran, can be used, Also in these, aromatic hydrocarbon, aliphatic hydrocarbon, alicycle fellows hydrocarbon, or ether currently industrially used widely is preferred.

[0040] Since norbornene system resin used for this invention is excellent in chemical resistance, some above-mentioned solvents are not dissolved. When using such a solvent, a polymerization or a hydrogenation reaction is performed in the state where a polymer etc. are distributing, or the state where it is dissolving in part. However, when it has the melting point, without a polymer having the melting point only after becoming a hydride, a polymerization and a hydrogenation reaction can also be performed in the state where a polymer is dissolving thoroughly. When polymerizing in an organic solvent, as for concentration of a monomer in a solution, 1 to 50 % of the weight is preferred, its 2 to 45 % of the weight is more preferred, and especially its 3 to 40 % of the weight is preferred. When concentration of a monomer is smaller than 1 % of the weight, there is fear that productivity is bad, when larger than 50 % of the weight, solution viscosity after a polymerization is too high, and a subsequent hydrogenation reaction may become difficult. A polymerization reaction is started by mixing a norbornene system monomer and a polymerization catalyst. Although polymerization temperature does not have restriction in particular, generally - 30 °C - 200 °C are 0 °C - 180 °C preferably. Polymerization time is for [1 minute] - 100 hours, and there is no restriction in particular. In this way, a norbornene system ring-opening-polymerization object which has the melting point produced by polymerizing is advanced to a mixing process of a combination drug etc. next with a state of volatile constituent removal processes, such as a solvent, or a solution, when using it for spinning as a norbornene system ring-opening-polymerization object. When using it for spinning as a norbornene system ring-opening-polymerization object hydride, it is transported to a hydrogenation reaction process for hydrogenation.

[0041] It is a reaction hydrogenated to a carbon-carbon double bond which exists in a main chain or/and a side chain, and hydrogenation of a norbornene system ring-opening-polymerization object is performed by supplying hydrogen in the system of reaction under existence of a hydrogenation catalyst. If it is generally used when hydrogenating an olefin compound as a hydrogenation catalyst, it will be usable and will not be restricted in particular, but the following is mentioned, for example. A catalyst system which consists of combination of a transition metal compound and an alkali metal compound as a homogeneous catalyst, For example, cobaltous acetate/triethylaluminum, nickel acetylacetonato / triisobutylaluminum, Combination of titanocene dichloride / n-butyl lithium, zirconocene dichloride / sec-butyl lithium, tetrabutoxy titanate / dimethylmagnesium, etc., etc. is mentioned. Noble metal complex catalysts, such as dichlorobis (triphenyl phosphine) palladium, a chloro hydride carbonyltris(triphenyl phosphine) ruthenium, and chlorotris(triphenyl phosphine) rhodium, can be mentioned.

[0042] As a heterogeneous catalyst, nickel, palladium, platinum, rhodium, a ruthenium, Or a solid catalyst which made carriers, such as carbon, silica, diatomite, alumina, and titanium oxide, support these metal, For example, a catalyst system of nickel/silica, nickel/diatomite, nickel/alumina, palladium/carbon, palladium/silica, palladium/diatomite, palladium/alumina, etc., etc. is mentioned. A hydrogenation reaction is usually carried out in an inert organic solvent. As

such an inert organic solvent, aromatic hydrocarbon; n-pentane, such as benzene and toluene, Aliphatic hydrocarbon, such as n-hexane; ether, such as alicyclic hydrocarbon; tetrahydrofurans, such as cyclohexane and a decalin, and ethyleneglycol dimethyl ether, etc. are mentioned.

[0043]What is necessary is for an inert organic solvent to be the same as a polymerization reaction solvent, and to add a hydrogenation catalyst in polymerization reaction liquid as it is, and just to make it usually react to it. Although a hydrogenation reaction differs in a condition range for which it is suitable by a hydrogenation catalyst system to be used, hydrogenation temperature -- usually -20°C -- -10 to 220°C 250 $^{\circ}\text{C}$ are 0 to 200 $^{\circ}\text{C}$ more preferably -- hydrogen pressure -- usually -- it is 0.1 -- 3 MPa more preferably 0.05 to 4 MPa 0.01 to 5 MPa. When hydrogenation temperature is too low, there is a possibility that reaction velocity may become slow, and if too high, a side reaction may occur. Since a high-withstand-pressure reaction apparatus is needed when too high [if hydrogen pressure is too low, hydrogenation speed will become slow, and], it is not desirable. A hydrogenation rate is usually preferred not less than 50% from a heat-resistant viewpoint, not less than 70%, more preferably, it is not less than 90% preferably, and hydrogenation reaction time can attain the above-mentioned hydrogenation rate especially not less than 80% in 0.1 to 10 hours.

[0044]In this invention, it can replace with norbornene system resin and a syndiotactic structure content styrene system polymer hydride can be used. As a syndiotactic structure content styrene system polymer, In a styrene system polymer, a special configuration with a polymer of structure which a side chain phenyl group (what has a substituent is included) arranges to an opposite hand by turns to a main chain of a polymer. It has tacticity by the ^{13}C -NMR not less than 50% preferably not less than 30% by not less than 85% or a pentad not less than 75% by die ADDO. Substituent content styrene which has a methyl group or an ethyl group to carbon of an alpha position which styrene and a phenyl group combine as a styrene system polymer, Or it is a copolymer which contains homopolymers or these monomers of substituent content styrene which has an alkyl group, an alkoxy group, or a halogen group of the carbon numbers 1-4 in a phenyl group 50% of the weight or more. They are a styrene homopolymer, a alpha-methylstyrene homopolymer, p-methylstyrene homopolymer, m-methylstyrene homopolymer, t-butylstyrene homopolymer, p-chlorostyrene homopolymer, or m-chlorostyrene homopolymer also in these.

[0045]A polymerization method of a syndiotactic structure content styrene system polymer polymerizes the above-mentioned monomer as a bond-products catalyst of a titanium compound and water, and trialkylaluminum in an inertness organic solvent or under absence of a solvent in the above-mentioned monomer (JP,62-167700,A). Mw of a syndiotactic structure content styrene system polymer, it is the gel permeation chromatography (polystyrene standard) which uses chloroform as a solvent -- usually -- 500-1,000,000 -- desirable -- 1,000-600,000 -- it is 5,000-400,000 more preferably. When Mw is too low, there is a possibility that a mechanical strength of fibrous mold goods may fall, conversely, if Mw is too high, melting mobility may get worse and spinning may become difficult.

[0046]In this invention, a double bond which exists in a main chain or a side chain by aromatic ring in a syndiotactic structure content styrene system polymer and a case is hydrogenated and used. A hydrogenation reaction of a syndiotactic structure content styrene system polymer can be performed like a hydrogenation reaction of the above-mentioned norbornene system ring-opening-polymerization object. a hydrogenation rate -- usually -- it is 90 % of the weight or more more preferably 70% of the weight or more 50% of the weight or more. There is a possibility that a degree of crystallinity will become low if there are too few hydrogenation rates, and heat resistance may fall. A syndiotactic structure content styrene system polymer hydride used for this invention has the melting point. The melting point is a temperature which a crystal part of a polymer dissolves. It can ask for the melting point with the above-mentioned measuring method etc. 130-400 $^{\circ}\text{C}$ of Tm(s) of a syndiotactic structure content styrene system polymer hydride are usually 200-400 $^{\circ}\text{C}$ preferably.

[0047]As for a reaction solution which a hydrogenation reaction of a norbornene system ring-opening-polymerization object or a syndiotactic structure content styrene system polymer

ended, a ** exception carries out catalysts for hydrogenation and a filter aid next. A polymer solution of the back according to ** is transported to a spinning process, since volatile constituents, such as a solvent, are removed and it is made charges of shaping material, such as a pellet, with another polymer and various combination drugs, or after mixing with other polymers or various combination drugs with solution states.

[0048]As a method of removing volatile constituents, such as a solvent, publicly known methods, such as the solidifying method and a direct drying method, are employable. Although the solidifying method is a method of depositing a polymer by mixing a polymer solution with a poor solvent of a polymer and a kind of poor solvent changes with the kinds of unsaturation ring vinyl polymerization object hydrogenation thing. For example, ketone, such as alcohols; acetone or methyl ethyl ketone, such as ethyl alcohol, n-propyl alcohol, or isopropyl alcohol; polar solvents, such as ester species, such as ethyl acetate or butyl acetate, can be mentioned. For example, it is made to heat and dry in a vacuum, nitrogen, or the air, and an ingredient of particle state acquired by solidifying is made into particle state, or is further extruded from a melting extrusion machine if needed, and is made into a pellet type. A direct drying method is a method of heating a polymer solution under decompression and removing a solvent. It can carry out to this method using a device with publicly known centrifugal thin film continuation evaporation drier, ** side heat exchange type successive reaction machine type dryer, hyperviscous reactor device, etc. By the device, a degree of vacuum and temperature are chosen suitably and are not limited.

[0049]Other polymers can be blended with norbornene system resin or a syndiotactic structure content styrene system polymer hydride used for this invention and used. A gum polymer and other thermoplastics are mentioned as other polymers. Glass transition temperature (it may be hereafter described as Tg.) of a gum polymer is a polymer 40 ** or less. Rubber and thermoplastic elastomer are contained in a gum polymer. When there is two or more glass transition temperature like a block copolymer, if the lowest glass transition temperature is 40 ** or less, in this invention, it can use as a gum polymer. Although Mooney viscosity (1+4,100 ** of ML(s)) of a gum polymer is suitably chosen according to the purpose of use, it is usually 5-300.

[0050]As a gum polymer, for example Ethylene-alpha olefin system rubber; ethylene-methyl methacrylate, copolymer [of ethylene, such as *****- butyl acrylate, and unsaturated carboxylic acid ester]; -- copolymer [of ethylene, such as ethylene-vinyl acetate, and fatty acid vinyl]; -- ethyl acrylate. Butyl acrylate, acrylic acid hexyl, 2-ethylhexyl acrylate, A polymer of acrylic acid alkyl ester, such as acrylic acid lauryl; Polybutadiene, Polyisoprene, styrene butadiene, or a random copolymer of styrene isoprene, An acrylonitrile butadiene copolymer, a butadiene isoprene copolymer, A butadiene (meta) acrylic-acid-alkyl-ester copolymer, a butadiene (meta) acrylic acid alkyl ester acrylonitrile copolymer, diene system rubber [, such as a butadiene (meta-) acrylic acid alkyl ester acrylonitrile styrene copolymer,]; -- butylene-isoprene copolymer; -- a styrene butadiene block copolymer. A hydrogenation styrene butadiene block copolymer, a hydrogenation styrene butadiene random copolymer, Aromatic vinyl conjugated diene system block copolymers, such as a styrene isoprene block copolymer and a hydrogenation styrene isoprene block copolymer, A low crystal polybutadiene resin, an ethylene-propylene elastomer, a SUCHIRENGURAFUTO ethylene-propylene elastomer, a thermoplastic polyester elastomer, ethylene system ionomer resin, etc. can be mentioned. A hydrogenation styrene butadiene block copolymer, a hydrogenation styrene isoprene block copolymer, etc. which are excellent in heat resistance and weatherability among these gum polymers are preferred. These gum polymers are independent, respectively, or can be combined two or more sorts and can be used.

[0051]Quantity of a gum polymer is suitably chosen according to the purpose of use. When shock resistance and pliability are required, quantity of a gum polymer, as opposed to norbornene system resin or syndiotactic structure content styrene system polymer hydride 100 weight section -- usually -- it is the range of one to 50 weight section more preferably 0.1 to 70 weight section 0.01 to 100 weight section. As other thermoplastics, for example Low density polyethylene, high density polyethylene, Straight-chain-shape low density polyethylene, ultra low density polyethylene, an ethylene-ethyl acrylate copolymer, An ethylene-vinylacetate copolymer, polystyrene, a polyphenylene sulfide, Polyphenylene ether, polyamide, polyester, polycarbonate,

cellulose triacetate, polyether imide, polyimide, polyarylate, polysulfone, polyether sulphone, etc. are mentioned. Thermoplastics of these others is independent, respectively, or can be used combining two or more sorts, and the blending ratio is suitably chosen in the range which does not spoil the purpose of this invention.

[0052] Various combination drugs generally used for norbornene system resin or a syndiotactic structure content styrene system polymer hydride used for this invention to a synthetic resin in the range which does not check the purpose of this invention may be added. As various combination drugs, stabilizer (antioxidant), an ultraviolet ray absorbent, a spray for preventing static electricity, a slipping agent, an antifogger, a color, paints, colorant, natural oil, synthetic oil, a plasticizer, an organic or inorganic bulking agent, an antimicrobial agent, a deodorizer, a deodorant, etc. are mentioned, for example.

[0053] As stabilizer, they are octadecyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl) propionate and tetrakis, for example. [Methylene-3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl) propionate] Methane, pentaerythrityl tetrakis [3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate] Which phenolic antioxidant; Triphenyl phosphite, tris (cyclohexylphenyl) phosphite, The Lynn system antioxidants, such as 9,10-dihydro-9-oxa 10-phosphorphenanthrene; The dimyristyl 3, 3'-thiodipropionate, Sulfur system antioxidants, such as distearyl 3,3'-thiodipropionate, lauryl stearyl 3,3'-thiodipropionate, and pentaerythritol tetrakis (beta-lauryl thio- propionate), etc. can be mentioned. Also in these, a phenolic antioxidant is preferred. These stabilizer is independent, respectively or can be used combining two or more sorts. Quantity of stabilizer is usually the range of 0.01 - the amount part of duplexes preferably 0.001 to 5 weight section to norbornene system resin [which is used for this invention], or syndiotactic structure content styrene system polymer hydride 100 weight section.

[0054] As an ultraviolet ray absorbent and weathering stabilizer, for example 2, 2, 6, and 6-tetramethyl 4-piperidyl benzoate, Bis(2,2,6,6-tetramethyl 4-piperidyl)sebacate, bis(1,2,2,6,6-pentamethyl 4-piperidyl)-2-(3,5-di-*t*-butyl-4-hydroxybenzyl)-2-*n*-butyl malonate, 4 - [3-(3,5-di-*t*-butyl-4-hydroxyphenyl) propionyloxy] -1-[2-[3-(3,5-di-*t*-butyl-4-hydroxyphenyl) propionyloxy] Hindered amine system compounds, such as ethyl-2,2,6,6-tetramethylpiperidine; 2-(2-hydroxy-5-methylphenyl) benzotriazol, A 2-(3-*t*-butyl-2-hydroxy-5-methylphenyl)-5-chlorobenzotriazole, A 2-(3,5-di-*t*-butyl-2-hydroxyphenyl)-5-chlorobenzotriazole, Benzotriazol system compounds, such as 2-(3,5-di-*t*-amyl 2-hydroxyphenyl) benzotriazol; 2,4-di-*t*-buthylphenyl 3,5-di-*t*-butyl-4-hydroxy benzoate, BEZOETO system compounds, such as hexadecyl-3,5-di-*t*-butyl-4-hydroxy benzoate, etc. are mentioned. These ultraviolet ray absorbents and weathering stabilizer are independent, respectively, or can be combined two or more sorts and can be used. Quantity of an ultraviolet ray absorbent and weathering stabilizer is usually the range of 0.01 - the amount part of duplexes preferably 0.001 to 5 weight section to norbornene system resin [which is used for this invention], or syndiotactic structure content styrene system polymer hydride 100 weight section.

[0055] As a spray for preventing static electricity, stearyl alcohol, long chain alkyl alcohol [, such as behenyl alcohol,]; -- sodium alkylsulfonate salt and/or alkyl-sulfonic-acid phosphonium salt; -- fatty-acid-ester [, such as glycerol ester of stearic acid,]; -- hydroxy amine compound; -- amorphous carbon and tin-oxide powder. Antimony content tin-oxide powder etc. can be illustrated. Quantity of a spray for preventing static electricity is usually the range of zero to 5 weight section to norbornene system resin [which is used for this invention], or syndiotactic structure content styrene system polymer hydride 100 weight section.

[0056] Norbornene system resin or a syndiotactic structure content styrene system polymer which desiccation ended, With other above-mentioned polymers and combination drugs, for example with a 2 axis kneading machine etc., after carrying out melt kneading at temperature of about 200-400 **, it is processed into a pellet, granulation, powder, etc., and melt spinning is presented as a charge of shaping material. Or this is dissolved in a solvent and wet spinning is presented. On the other hand, wet spinning can also be presented, after mixing with a polymer of above others, or a combination drug by solution states after a polymerization, or solution states after a hydrogenation reaction and considering it as a solution form charge of shaping material, as described above.

[0057] Melt spinning is the method of making it filar, heating a polymer to temperature of less than decomposition temperature, and more than that melting point making it into a molten state, and extruding and taking it over from a spinneret (fine pores), giving a crystal structure to a polymer in this process, cooling, and rolling round. Although norbornene system resin and a syndiotactic structure content styrene resin hydride which are used for this invention have the comparatively high melting point and heat resistance is high, it has the feature which becomes hypoviscosity remarkably among 200–400 **, and serves as mobility. Although this reason is not clear, since it has crystallinity, it will be in a liquid crystal state and it is thought that viscosity falls rapidly. Therefore, it is possible to fabricate for a short time to fibrous, since it flows well in spite of being resin with high melting temperature, and norbornene system resin and a syndiotactic structure content styrene resin hydride which are used for this invention are **.

[0058] It is the method of drying and removing a solvent, wet spinning extruding a solution containing a polymer, a combination drug, etc. in a coagulation solvent from a spinneret, elongating a line of thread, and giving a crystal structure to a polymer in this process. As a solvent added to a charge of shaping material which could use a solvent used for a polymerization reaction, and a solvent used for a hydrogenation reaction as it was, and a pellet etc. dried, a solvent illustrated to a solvent for polymerization reactions can be used for a solvent used for wet spinning. As a coagulation solvent, alcohols, ketone, ester species, etc. which are the poor solvents used for coagulation of the aforementioned polymer hydride can be used.

[0059] Norbornene system resin or a syndiotactic structure content styrene system polymer hydride with which fibrous mold goods are presented in this invention, Since it is a polymer which has the melting point, i.e., a polymer which forms a crystal structure, also in melt spinning, it becomes flexibility polymers which form a crystal part and in which this and an amorphism part have aesthetic property conjointly in it inside fibrous mold goods when a polymer is extruded from fine pores also in wet spinning. Fibrous mold goods of this invention can also be manufactured by performing norbornene system resin or a syndiotactic structure content styrene system polymer hydride, a polymer of a different kind, and compound spinning. There may be a junction spinning method and a sheath-core spinning method in a method of compound spinning, and any may be sufficient. A junction spinning method is the method of carrying out spinning of the shape of melting, or two sorts of solution form polymers simultaneously from two divided spinnerets, pasting both together in a cap discharge part, and making it into one textiles. A sheath-core spinning method is the method of carrying out a co-extrusion as a delivery of structure through which one polymer encloses the surroundings of a polymer of another side, and flows. As an example of the other party's polymer to compound, a gum polymer in which the above-mentioned combination is possible, and other thermoplastics are mentioned. Fibrous mold goods of this invention can also be considered as shape in the air. How to provide a mandrel in delivery gold and carry out the regurgitation of the shape of melting, or the solution form polymer to it in shape of extraction as a method of obtaining a hollow fiber, There are a method of joining mutually according to a Barus effect in which melt of a polymer or a flow of a solution which came out of 3–5 delivery gold arranged to circumference shape swells, and making a centrum form, etc.

[0060] In order to raise a degree of crystallinity that a mechanical strength of fibrous mold goods should be increased, it extends preferably. Extension is elongating fibrous mold goods formed with spinning about 2 to 7 times, and giving plastic deformation. This plastic deformation is friction of an inside and has an effect which also extends an amorphous chain and carries out orientation in the direction of a fiber axis as well as a crystal chain. A temperature desirable although extended is below T_m above T_g . Heat-treating is also preferred. Heat treatments are temperature below T_m , and the operation which is $-(T_g+10^{**})$ (T_m-20^{**}) preferably, and is held for 10 minutes – several hours above T_g , and there are effects, such as relaxation of internal distortion of a drawn fiber and promotion of crystallization.

[0061] thus, a diameter of fibrous mold goods of obtained this invention -- usually -- it is 0.0001–0.1 mm more preferably 0.0001–0.5 mm 0.0001–1 mm. Fibrous mold goods of norbornene system resin of this invention or a syndiotactic structure content styrene system polymer

hydride are excellent in heat resistance and chemical resistance, and its mechanical strengths, such as tensile strength, are large. Since pyrolysis temperature is high, it has an advantage with a wide working temperature range. Since especially fibrous mold goods of a norbornene system ring-opening-polymerization object hydride are excellent in heat resistance, tensile strength, a tension elastic modulus, etc., they are especially preferred. It can be made a textile, without carrying out throwing, and can use for a nonwoven fabric, a filter cloth, etc., and throwing of the fibrous mold goods of this invention which has these features is carried out thickly, and they are used as textile fabrics, they can be made into **** and are applicable to a rope, a package string, a fishing net, a network, etc. in tentorium, sail cloth, various bagging, etc. again. Since norbornene system resin of this invention or a syndiotactic structure content styrene system polymer hydride is excellent also in transparency while it is crystallinity, it can be used also for textiles for optics, such as an optical fiber.

[0062]

[Example]An example and a comparative example are given to below, and this invention is explained to it still more concretely. The examining method was depended below. Hereafter, the part in an example and a comparative example and % are weight references, unless it mentions specially.

(1) The weight average molecular weight (Mw) and the number average molecular weight (Mn) of the norbornene system ring-opening-polymerization object were measured, respectively as a standard polystyrene reduced property by the gel permeation chromatography (GPC) which uses chloroform as a solvent.

(2) The hydrogenation rate was measured by the infrared absorption spectrum.

(3) With the differential scanning calorimeter (DSC), by a part for 10 **/, temperature up of the melting point (Tm) and the glass-transition temperature (Tg) was carried out, and they were measured.

[0063](4) Thermo gravity reduction starting temperature measured the fibrous mold goods 10g according to JISK 7120 in a nitrogen atmosphere.

(5) The examination of the tensile strength of fibrous mold goods and a tension elastic modulus was based on ASTM D638.

[0064](6) The chemical corrosion resistance test of fibrous mold goods ten textiles 30 cm in length each the standard which describes below the result which it immersed each in acetone, toluene, cyclohexane, a carbon tetrachloride, chloride (35% of concentration), and 200 ml of ammonia solutions (28% of concentration) at 23 ** for 24 hours, respectively, was taken out, and was observed -- a sign -- a table -- the bottom.

O : there is no appearance change of swelling, the dissolution, etc. There is also no tensile strength fall.

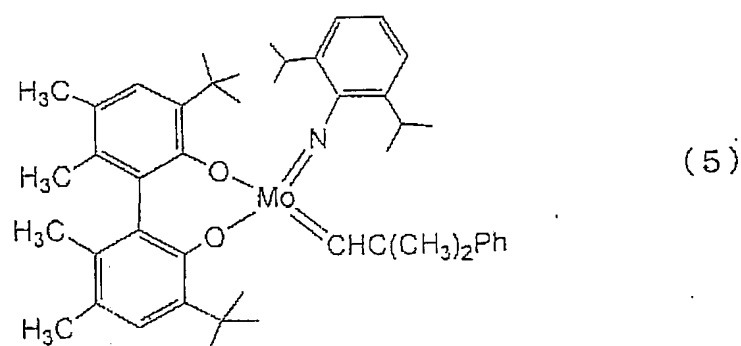
** : Swelling is seen a little. Or shape has collapsed. The degree of fall of tensile strength is 0 to 50%.

x : It is mostly dissolving thoroughly. The degree of fall of tensile strength is over 50%.

[0065]After adding 0.0068 copy of molybdenum compound shown in a glass reactor with example 1 agitator by a general formula (5), 24 copies of cyclohexane, six copies of dicyclopentadienes, and 0.00573 copy of 1-hexene were added, and the polymerization reaction was performed at the room temperature.

[0066]

[Formula 5]



[0067]The white sediment deposited in an instant after the polymerization reaction start. After a 3-hour reaction, a lot of isopropanols were filled with polymerization reaction liquid, polymer was deposited thoroughly, and reduced pressure drying was carried out at 40 ** after [classified by **] washing for 40 hours. The yield of the acquired norbornene system ring-opening-polymerization object was 5.5 copies, and were Mw103,000 and Mn37,000. Tm was 218 ** and Tg was 95 **. Subsequently, it is hindered phenolic antioxidant pentaerythrityl tetrakis to these 100 copies of ring-opening-polymerization objects. 0.2 copy of [3-(3,5-di-tertiary-butyl-4-hydroxyphenyl) propionate] was added, with the twin screw extruder, melt kneading was carried out with the resin temperature of an average of 320 **, it pelletized by the pelletizer, and the charge of shaping material was obtained. The nozzle block for spinning which made this pellet connect with melting, extrusion, and an extrusion machine with an extrusion machine {barrel temperature of 310 ** and die temperature of 320 **} was passed, and it rolled round, having used thread 0.1 mm in diameter through oiling, and cooling in a tank, and fibrous mold goods were obtained. Spinning speed was 200 m/min. Subsequently, about these fibrous mold goods, heat treatment held for 3 minutes at 160 ** was performed. The tensile strength of fibrous mold goods was 1.1GPa, and the tension elastic moduli were 7.9GPa. The starting temperature of thermo gravity reduction was 360 **. In the chemical corrosion resistance test, there is no appearance change of swelling, the dissolution, etc. and strength reduction was also looked at by neither.

[0068]5.0 copies of ring-opening-polymerization objects and 88 copies of cyclohexane which were produced by performing the same reaction as Example 1 to autoclave with example 2 agitator were added. Subsequently, the hydrogenation catalyst solution which dissolved 0.031 copy of bis(tri-cyclohexyl phosphine)benzylidyne ruthenium (IV) dichloride and 1.8 copies of ethyl vinyl ether in 18 copies of cyclohexane is added, The hydrogenation reaction was performed at hydrogen pressure 0.785MPa and the temperature of 120 ** for 10 hours. After the reaction, a lot of isopropanols were filled with reaction mixture, and after depositing polymer thoroughly and a ** exception's washing it, reduced pressure drying was carried out at 40 ** for 40 hours. The absorption of carbon-carbon double bond origin was not observed by the infrared absorption spectrum, but the hydrogenation rate was not less than 99%. Tm of the obtained norbornene system ring-opening-polymerization object hydride was 272 **, and Tg was 102 **. Henceforth, the pellet was produced like Example 1 using this norbornene system ring-opening-polymerization object hydride, and shaping and heat treatment of fibrous mold goods were performed. The diameter of fibrous mold goods was 0.1 mm, and were tensile strength 1.3GPa and tension elastic-modulus 8.2GPa. The starting temperature of thermo gravity reduction was 400 **. In the chemical corrosion resistance test, there is no appearance change of swelling, the dissolution, etc. and strength reduction was also looked at by neither.

[0069]In example 3 Example 2, when obtaining fibrous mold goods, after taking over carried out extension 3 times more quickly than an extrusion rate, it heat-treated, and also carried out like Example 2. The diameter of fibrous mold goods was 0.06 mm, and were tensile strength 0.2GPa and tension elastic-modulus 20GPa. The starting temperature of thermo gravity reduction was 400 **. In a chemical corrosion resistance test, there is no appearance change of swelling, the dissolution, etc. and strength reduction was not seen, either.

[0070]In comparative example 1 Example 1, using the pellet of the syndiotactic polystyrene

(second-PS) of Tg96 ** and Tm270 ** as a charge of shaping material, changed barrel temperature into 290 **, and die temperature was changed into 300 **, respectively, and also fibrous mold goods were obtained like Example 1. Subsequently, about these mold goods, heat treatment held for 3 minutes at 160 ** was performed. The diameter of fibrous mold goods was 0.1 mm, and were tensile strength 0.8GPa and tension elastic-modulus 5GPa. The starting temperature of thermo gravity reduction was 300 **. Due to the chemical corrosion resistance test, although change was not looked at by the hydrochloric acid aqueous solution, it dissolved in toluene and a carbon tetrachloride, it swelled to acetone, cyclohexane, and an ammonia solution, and shape collapsed.

[0071]In the comparative example 2 comparative example 1, after obtaining fibrous mold goods, this was heat-treated after performing extension 3 times at the temperature of 150 **, and also it carried out like the comparative example 1. The diameter of fibrous mold goods was 0.06 mm, and were tensile strength 0.12GPa and tension elastic-modulus 12GPa. The starting temperature of thermo gravity reduction was 300 **. The chemical corrosion resistance test was the same as that of the comparative example 1.

[0072]In comparative example 3 Example 1, using the pellet of high density polyethylene of Tg-125 ** and Tm135 ** as a charge of shaping material, changed barrel temperature into 300 **, and die temperature was changed into 210 **, respectively, and also fibrous mold goods were obtained like Example 1. Subsequently, about this Plastic solid, heat treatment held for 3 minutes at 80 ** was performed. The diameter of fibrous mold goods was 0.1 mm, and were tensile strength 0.5GPa and tension elastic-modulus 4GPa. The starting temperature of thermo gravity reduction was 300 **. In a chemical corrosion resistance test, there is no appearance change of swelling, the dissolution, etc. also in any, and strength reduction was not seen, either.

[0073]In comparative example 4 Example 1, using the pellet of the polyamide (nylon 6) of Tg72 ** and Tm215 ** as a charge of shaping material, changed barrel temperature into 250 **, and die temperature was changed into 260 **, respectively, and also fibrous mold goods were obtained like Example 1. Subsequently, about this Plastic solid, heat treatment held for 3 minutes at 150 ** was performed. The diameter of fibrous mold goods was 0.1 mm, and were tensile strength 0.075GPa and tension elastic-modulus 2.4GPa. The starting temperature of thermo gravity reduction was 300 **, there having been swelling a little to cyclohexane, and also also setting to any in a medicine-proof examination, -- completeness -- or it mostly dissolved. The result of Examples 1-3 and the comparative examples 1-4 is described in Table 1.

[0074]

[Table 1]

表 1

	実施例 1	実施例 2	実施例 3	比較例 1	比較例 2	比較例 3	比較例 4
延伸倍率	1	1	3	1	3	1	1
繊維状成形品の直径 (mm)	0.1	0.1	0.06	0.1	0.06	0.1	0.1
ガラス転移温度 (°C)	95	102	102	96	96	-125	72
融点 (°C)	218	272	272	270	271	135	215
熱重量減少開始温度 (°C)	360	400	400	300	300	300	300
引張強度 (GPa)	1.1	1.3	0.2	0.8	0.12	0.5	0.075
引張り弾性率 (GPa)	7.9	8.2	20	5	12	4	2.4
耐薬品性	アセトン	○	○	△	△	○	×
	トルエン	○	○	×	×	○	×
	シクロヘキサン	○	○	△	△	○	△
	四塩化炭素	○	○	×	×	○	×
	(酸)	○	○	○	○	○	×
	(アルカリ)	○	○	△	△	○	△

[0075]As shown in Table 1, the fibrous mold goods of this invention obtained using the norbornene system ring-opening-polymerization object which has the melting point, and its hydride, Thermo gravity reduction starting temperature was high, heat resistance was good, and

was not invaded by an organic solvent, acid, and alkali, it excelled in chemical resistance, and tensile strength and a tension elastic modulus were also very large values between the textiles of the same thickness. (Examples 1-3). On the other hand, heat resistance and chemical resistance were inferior to the fibrous mold goods of this invention in conventional fibrous mold-goods s-PS irrespective of the existence of extension, and the mechanical strength was also low (comparative examples 1 and 2). Heat resistance and chemical resistance are inferior to the fibrous mold goods of this invention in nylon 6 like s-PS, and a mechanical strength is further inferior in it (comparative example 4). The polyethylene fiber was inferior to heat resistance and a mechanical strength, although solvent resistance was equivalent to fibrous ***** of this invention (comparative example 3).

[0076]

[Effect of the Invention]The fibrous mold goods which are excellent in heat resistance and chemical resistance, and consist of the norbornene system ring-opening-polymerization object, its hydride, or syndiotactic structure content styrene system polymer hydride of high intensity by this invention are provided.

[Translation done.]